

PATENT SPECIFICATION

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(54) POLYENES

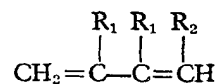
- (71) We, MITSUBISHI CHEMICAL INDUSTRIES LIMITED, a Japanese Company, of 2—5—2 Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 5 The invention relates to a method for the production of a substance resulting from the addition reaction between a 1,3-conjugated diene and a derivative of a dimer of a butadiene and to such substance. More particularly, the invention relates to a method for the production of a substance resulting from the addition reaction between a 1,3-conjugated diene and a straight-chain dimer of a butadiene, said dimer having a substituent group attached to the 1- or 3-position. The term "butadiene" is used in this specification to designate 1,3-butadiene and its homologues having a substituent alkyl group attached to carbon atom of the 2- or 3-position, and the term "1,3-conjugated diene" is applied to all those compounds which contain 1,3-conjugated diene bonds, for example, a butadiene as hereinbefore defined and 1,3,7-octatriene.
- 10 Methods are known for the production of dimers of a butadiene and derivatives thereof. For example, it is known to produce a straight-chain octatriene by the dimerisation of a butadiene using palladium acetate and triphenylphosphine as catalyst. It is also known to react a butadiene in the presence of said catalyst with an active hydrogen-containing compound such as an alcohol, phenol, carboxylic acids, a primary amine or a secondary amine thereby to produce a derivative of a straight chain dimer of a butadiene, in which derivative the active hydrogen-containing compound has added on to the carbon atom

at the 1- or 3-position of the straight-chain dimer. However, there has been no disclosure of a method for the selective production of derivatives of an oligomers of a butadiene which may be a trimer or a tetramer. Since these compounds contain at least 12 carbon atoms and have at least three carbon-carbon double bonds in the molecule, there is a wide field for their use as raw materials in the manufacture of synthetic drying oils, unsaturated alkyd resins or surfactants.

It is an object of the invention to provide a method for the production of a substance resulting from the addition reaction between a compound having 1,3-conjugated diene bonds and a compound having a structure such that a hydroxy group, alkoxy group, aryloxy group or acyloxy group is attached to the carbon atom at the 1- or 3-position of a straight-chain dimer of a butadiene.

It is another object of the invention to provide a method for the production of a derivative of a butadiene oligomer or co-oligomer which may be a trimer or a tetramer.

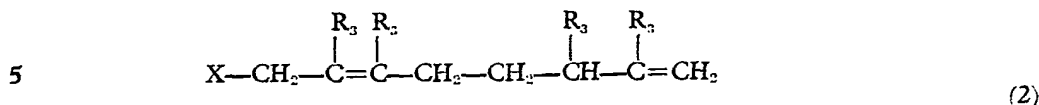
According to the invention there is provided a method for the production of an alkapolienyl group containing substance in which a molecule of a 1,3-conjugated diene is linked to an alkadienyl group containing compound and which substance has at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, which method comprises reacting (i) a 1,3-conjugated diene represented by the formula



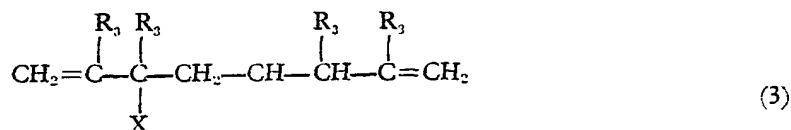
(1)

in which the R₁'s may be the same or different and each denotes hydrogen or an alkyl group

and R_2 denotes hydrogen, an alkyl group or an alkenyl group, with (ii) an alkadienyl group containing compound which is a 1-substituted-2,7-alkadiene represented by the formula



or a 3-substituted-1,7-alkadiene represented by the formula



10 in which the R_3 's may differ from one another, each R_3 denoting hydrogen or an alkyl group, and X denotes a hydroxy group, an alkoxy group, an arloxy group or an acyloxy group, the reaction being carried out in the presence of a rhodium compound as catalyst.

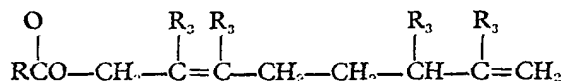
15 The 1,3-conjugated diene having the formula (1) for use as starting material in the method of the invention may be a butadiene, for example 1,3-butadiene, isoprene, or 2,3-dimethylbutadiene. Also, it may be a com-

20 pound, such as piperylene, in which the carbon atom at the 4-position of 1,3-butadiene has a substituent alkyl group. Further, it may be 1,3,7-octatriene, 2,6-dimethyl-1,3,7-octatriene, 2,7-dimethyl-1,3,7-octatriene or other compound in which the carbon atom at the 4-position in 1,3-butadiene has a substituent alkenyl group.

The preferred 1,3-conjugated diene compounds are 1,3-butadiene, isoprene and 1,3,7-octatriene, 1,3-butadiene being particularly preferred. 30

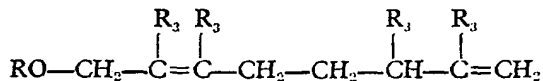
The term "alkadienyl group containing compounds" indicated by the formula (2) or (3) is applied to esters, ethers, and alcohols which are derivatives of straight-chain dimers of a butadiene. 35

According to the invention, furthermore, there is provided a method for the production of an alkapolyenyl group containing ester having at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, which comprises reacting an alkadienyl ester represented by the formula 40



45 in which R denotes an alkyl group or an aryl group and each R_3 denotes hydrogen or an alkyl group, the R_3 's being the same or different, with 1,3-butadiene, isoprene or a straight-chain dimer of 1,3-butadiene or isoprene, the reaction being carried out in the presence of a rhodium compound as catalyst.

The invention also provides a method for the production of an alkapolyenyl group containing ether having at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, which method comprises reacting an alkadienyl ether represented by the formula 55



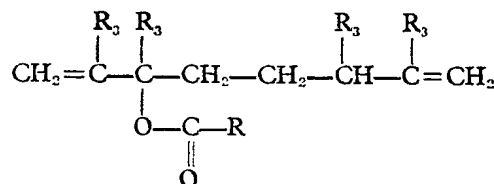
60 in which R denotes an alkyl group or an aryl group, and each R_3 denotes hydrogen or an alkyl group, the R_3 's being the same or otherwise, with 1,3-butadiene, isoprene, or a

straight-chain dimer of 1,3-butadiene or isoprene, the reaction being carried out in the presence of a rhodium compound as catalyst. 65

The invention also includes a method for

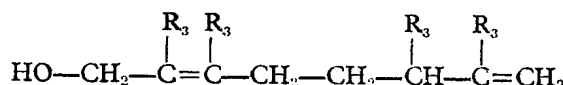
the production of an alkapolienyl group containing ester having at least 12 carbon atoms and at least 3 carbon-carbon double bonds in

the molecule, which comprises reacting an alkadienyl ester represented by the formula 5



in which R denotes an alkyl group or an aryl group, and each R₃ denotes hydrogen or an alkyl group, the R₃'s being the same or otherwise, with 1,3-butadiene, isoprene or a straight-chain dimer of 1,3-butadiene or isoprene, the reaction being carried out in the presence of a rhodium compound as catalyst.

According to the invention, moreover, a method for the production of an alkapolienyl group containing alcohol having at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, comprises reacting an alkadienyl alcohol having the formula 15

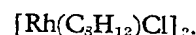


in which each R₃ is hydrogen or an alkyl group, the R₃'s being the same or otherwise, with 1,3-butadiene, isoprene or a straight chain dimer of isoprene or 1,3-butadiene, the reaction being carried out in the presence of a rhodium compound as catalyst.

such compounds having an alkadienyl group include 1-acetoxy-2,7-octadiene, 1-methoxy-2,7-octadiene, 1-phenoxy-2,7-octadiene, 1-hydroxy-2,7-octadiene, 3-acetoxy-1,7-octadiene, 3-methoxy-1,7-octadiene, 3-phenoxy-1,7-octadiene, and 3-hydroxy-1,7-octadiene which are derivatives of 1,3-butadiene dimer. Further, derivatives of isoprene dimer which correspond to these are also preferred, and among them 1-acetoxy-2,7-octadiene is the most preferred.

Esters and ethers, among alkadienyl group containing compounds, may readily be produced by a known method in which a butadiene is reacted with a carboxylic acid, alcohol or phenol. For example, the reaction of 1,3-butadiene with a carboxylic acid such as acetic acid, propionic acid, n-butyric acid, or benzoic acid in the presence of a catalyst comprising palladium acetate and triphenylphosphine gives a 1-acyloxy-2,7-octadiene and/or a 3-acyloxy-1,7-octadiene. The employment of an alcohol such as methanol, ethanol or allyl alcohol, or a phenol such as monohydroxybenzene or a cresol, in place of the carboxylic acid, gives a 2,7-octadiene and/or a 1,7-octadiene having an alkoxy group or a phenoxy group attached at the 1- or 3-position. Further, the employment of isoprene in place of 1,3-butadiene in these reactions, gives the same ester or ether except it has two methyl groups as side-chains. In this case, the two methyl groups are linked to carbon atoms at the 2- and 6-positions or at the 2- and 7-positions. The employment of a butadiene other than 1,3-butadiene and isoprene also gives esters or ethers corresponding to those produced from 1,3-butadiene. Further, an alkadienyl alcohol is produced by hydrolysing the acyloxyalkadienes manufactured in the manner mentioned. Preferred examples of

The method of the invention employs a rhodium compound as catalyst, which catalyst may be an inorganic or organic salt or organic complex of rhodium. Examples of such rhodium compounds include inorganic salts of rhodium such as rhodium chloride, rhodium bromide and rhodium nitrate, carboxylic acid salts of rhodium such as rhodium acetate and rhodium propionate, chelate compounds of rhodium such as rhodium acetylacetonate, π -allyl-type complexes of rhodium such as π -allyl-rhodium chloride, and other rhodium complexes such as tetrakis (ethylene)-dichloro dirhodium [Rh(C₂H₄)₂Cl]₂, bis (cycloocta-1,5-diene) dichloro dirhodium

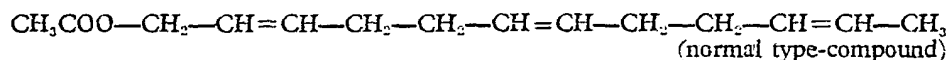
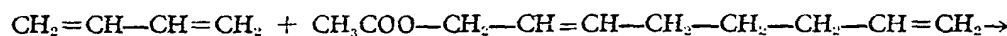


Rhodium chloride, RhCl₃·3H₂O, is particularly preferred. These rhodium compounds may be added directly to the reaction system, but their use as a solution in an alcohol facilitates the reaction and brings about better results. To this end, a primary alcohol such as methanol, ethanol or isopropanol is preferred.

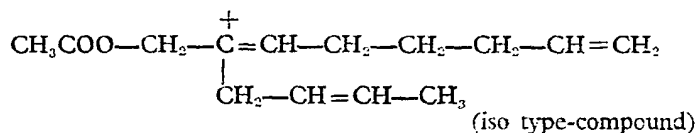
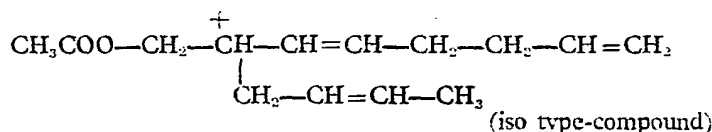
ably employed as a solvent for the catalyst.

According to the invention, the reaction between a 1,3-conjugated diene represented by the formula (1) and an alkadienyl compound having a substituent group at the 1-position, represented by the formula (2) in the presence of a rhodium compound gives rise mainly to a straight-chain substance the structure of which results from the linking of the carbon atom at the 8-position of 1-substituted alkadiene to the terminal carbon atom of the carbon chain of

the 1,3-conjugated diene compound and a substance the structure of which results from the carbon atom at the 2-position of 1-substituted alkadiene being linked to the terminal carbon atom of the carbon chain of the 1,3-conjugated diene. The former substance will hereinafter be referred to as "normal type-compound" and the latter as "iso type-compound." For example, the above mentioned reaction occurs between 1,3-butadiene and 1-acetoxy-2,7-octadiene as follows:



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Further, it is believed that the employment of an alkadienyl compound represented by the formula (3) as the alkadienyl group containing compound which has a substituent group at the 3-position gives mainly a substance the structure of which results from the linking of the carbon atom at the 7-position of the 3-substituted alkadiene to the carbon atom at the 1-position of the 1,3-conjugated diene and possibly a substance the structure of which arises from the linking of the carbon atom at the 1- or 2-position of the 3-substituted alkadiene to the carbon atom at the 1-position of the 1,3-conjugated diene.

Since the reaction of a n - α -olefin with a conjugated diene normally results in the formation of a linkage between the carbon atom at the 2-position of n - α -olefin and the conjugated diene, it was surprising to discover that in the case of a 1-substituted- n -octadiene or 3-substituted- n -octadiene in the method of the invention a conjugated diene linked to the terminal carbon atom of a chain or to a carbon atom constituting part of an internal carbon-carbon double bond.

The production of the said substance resulting from the reaction of a 1,3-conjugated diene with a derivative of a dimer of a butadiene may be effected in various ways according to the invention. For example, a 1,3-conjugated diene such as 1,3-butadiene, an alkadienyl group containing compound such as 1-acetoxy-2,7-octadiene and a catalyst such as rhodium chloride are charged into a reactor

such as an autoclave and held at a temperature in the range 50°C — 250°C , advantageously in the range 70°C — 200°C and preferably in the range 100°C — 130°C , with stirring for a period of from several tens of minutes to several hours, preferably in inert environment. The reaction may take place under autogenous pressure.

The 1,3-conjugated diene and the alkadienyl group containing compound are normally charged into a reactor in a ratio of 0.1—10 moles of the former to 1 mole of the latter. The rhodium compound used as catalyst is suitably employed in an amount of 10^{-4} to 10^{-2} mole per mole of the alkadienyl group containing compound.

In effecting the reaction, the reactants may be used in bulk or in solution in a solvent. Examples of suitable solvents include alcohols, such as ethanol, organic acids, such as acetic acid, hydrocarbons, such as benzene, ketones, such as acetone, and other various types of solvent that are inert in the reaction, such as methylene dichloride, tetrahydrofuran, and acetonitrile. Amide type-aprotic polar solvents such as dimethylformamide, dimethylacetamide pyrrolidone, N -methyl pyrrolidone, and tetramethyl urea may be employed. Further, in order to obtain better results from the reactions, a polymerisation inhibitor such as t -butylcatechol or phenothiazine or a titanium compound such as tetrabutoxy titanium and titanium tetrachloride may be added. When a 1-substituted-alkadiene represented by

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the formula (1) is employed as the alkadienyl group containing compound, the addition of a trivalent phosphorus compound, such as triphenylphosphine, tri-n-butylphosphine, triisopropylphosphine, tricyclohexylphosphine, phenyldichlorophosphine, phosphorus trichloride or triphenylphosphite, to the reaction system brings about an increase in the normal type-compound/iso-type compound ratio, that is, the production of the former increases.

The novel compounds produced according to the method of the invention and which are set forth in the claims, find extensive use as or for the production of intermediates. For example, hydrolysis of the esters gives unsaturated higher alcohols, and hydrogenation hydrolysis gives saturated higher alcohols. These substances may be converted via other reactions to surfactants. Further, the novel compounds are directly used as raw material from which various resinous materials, such as synthetic drying oils or modified alkyd resins may be produced.

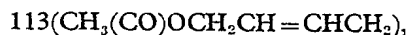
The invention is illustrated in the following examples:—

Example 1

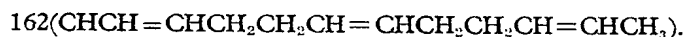
0.13 g (0.5 mmol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ dissolved in 0.92 g (20 mmol) ethanol and 33.6 g (0.2 mol)

1-acetoxy-2,7-octadiene were charged into a 100 c.c. autoclave. 21.6 g (0.4 mol) 1,3-butadiene were added thereto and the mixture was reacted at 110°C for 4 hours. Upon completion of the reaction, the autoclave was purged of unreacted 1,3-butadiene, giving 44.9 g reaction liquor. The reaction liquor was distilled and analysed by gas-chromatography; it was found to be composed chiefly of two components, namely, A-component having a boiling point of $77-86^\circ\text{C}/2\text{mmHg}$ and B-component having a boiling point of $96-101^\circ\text{C}/2\text{mmHg}$.

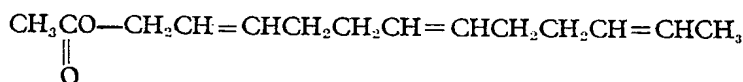
Infrared analysis of the B-component showed the absorption of $\text{C}=\text{O}$ of the acetoxy group at 1730 cm^{-1} and the absorption of an ether bond at 1220 cm^{-1} with no absorption indicating the presence of terminal vinyl group, whilst showing an absorption indicative of the presence of an inner olefin. An infrared spectrum of the B-component after being subjected to hydrogenation with subsequent hydrolysis, was identical with that of n-1-dodecanol. From this it was inferred that the B-component was a straight-chain compound having a terminal acetoxy group. A mass analysis of the B-component indicated absorptions at M/e $43(\text{CH}_3\text{CO})$, $61(\text{CH}_3(\text{CO})\text{OH}_2)$,



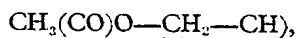
and



As the infrared analysis did not show a terminal vinyl group, the B-component was assumed to have the structure represented by the formula



A further analysis of the B-component by NMR (Nuclear Magnetic Resonance) using TMS as standard indicated absorptions at δ 16 (terminal methyl, CH_3-), δ 1.9 (methyl of acetoxy group, $\text{CH}_3(\text{CO})\text{O}-$), δ 2.1 (methylene, $-\text{CH}_2-$), δ 4.45 (doublet; methylene linked to acetoxy group,



and δ 5.4 (vinylic hydrogen, $=\text{CH}-$). From these facts it was concluded that the B-component was the compound represented by the above formula, that is, 1-acetoxy-2,6,10-dodecatriene (normal type-compound). Gas-chromatographic analysis indicated that the B-component was a mixture of the cis and transomers of 1-acetoxy-2,6,10-dodecatriene.

As to the A-component, a mass analysis after hydrolysis indicated no absorption of M/e 87 ($\text{CH}_3(\text{CO})\text{OCH}_2\text{CH}_2$), instead an absorption at 73 ($\text{CH}_2(\text{CO})\text{OCH}_2$) and



so implying that a butyl group was present as a side-chain. Further analysis by means of NMR indicated absorptions at δ 0.9 (terminal methyl, CH_3-), δ 1.3 (methylene, $-\text{CH}_2-$), δ 1.96 (methyl of acetoxy group,



and δ 3.9 (doublet; methylene linked to acetoxy group, $\text{CH}_3(\text{CO})\text{O}-\text{CH}_2-\text{CH}-$). As the absorption at δ 3.9 was doublet, only one

hydrogen atom was linked to the carbon atom linked to acetoxy-methyl group, indicating the linking of a butyl group to said carbon atom as a side-chain. From these observations it was deduced that the A-component should be a compound of such structure that it had an acetoxy group at the 1-position and a buta-

diene linked at the 2-position.

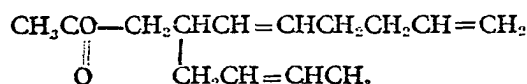
The A-component was immediately separated into further two components, A—1 and A—2, by means of gas-chromatographic analysis. A mass analysis of the A—1 component showed absorptions at M/e



and 125 ($\text{CH}_3(\text{CO})\text{OCH}_2\text{CHCH}=\text{CHCH}_2$), and a NMR analysis showed absorptions at δ 1.6 (terminal methyl, CH_3-), δ 1.9 (methyl of acetoxy group, $\text{CH}_3(\text{CO})\text{O}-$), δ 2.1 (methylene, $-\text{CH}_2-$), and δ 3.9 (doublet); methylene linked to acetoxy group,



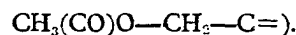
Thus, the A—1 component was deduced to be 1-acetoxy - 2 - (2' - butenyl) - 3,7 - octadiene (iso type-compound) represented by the formula



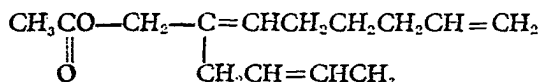
A mass analysis of the A—2 component showed an absorption at M/e



and no absorption at M/e 167 the elimination of butyl group, implying that there were double bonds at carbon atoms to which a side-chain was attached. Further, a NMR analysis showed absorptions at δ 1.6 (terminal methyl, CH_3-), δ 1.9 (methyl of acetoxy group, $\text{CH}_3(\text{CO})\text{O}-$), δ 2.1 (methylene, $-\text{CH}_2-$), δ 2.6 (methylene between two adjacent double bonds, $=\text{C}-\text{CH}_2-\text{C}=\text{C}$), and δ 4.5 (singlet; methylene linked to acetoxy group



In view of the fact that the absorption at δ 4.5 was singlet, it was inferred that no hydrogen was attached to the carbon atom linked to the acetoxymethyl group, and in view of the absorption at δ 2.6, it was inferred that the A—2 component should be 1 - acetoxy - 2 - (2' - butenyl) - 2,7 - octadiene (iso type-compound) represented by the following formula:



The reaction liquor was composed of 21.0 g of 1-acetoxy-2,6,10-dodecatriene, 14.4 g of 1-acetoxy-2-(2'-butenyl)-3,7-octadiene and 1-acetoxy-2-(2'-butenyl)-2,7-octadiene, and 6.1 g of unreacted 1-acetoxy-2,7-octadiene, indicating a 81.8% conversion of 1-acetoxy-2,7-octadiene, a 97.6% selectivity of reaction products and a 1.46 ratio of normal type-compound to iso type-compound.

Example 2

The same method as in Example 1 was followed for reacting 1,3-butadiene with 1-acetoxy-2,7-octadiene over 0.13 g $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in solution in 0.92 g ethanol in the presence of various additives. The reaction conditions and the results of the reaction are shown in the following Table 1.

TABLE 1

Run	1	2	3	4
1,3-butadiene, mol	0.4	0.1	0.2	0.2
1-acetoxy-2,7-octadiene, mol	0.2	0.2	0.2	0.2
Additive Kind	1-butyl-catechol	ditto	ditto	ditto
mg	20	20	20	20
Reaction temp., °C	110	120	80	140
Reaction period, hr	2	5	5	0.25
*1 Conversion, %	87.2	31.0	54.7	78.3
*2 Selectivity, %	72.7	78.0	100	83.7
*3 n/iso ratio	1.77	2.26	1.50	1.38

TABLE 1 (Continued)

Run	5	6	7
1,3-butadiene, mol	0.4	0.2	0.4
1-acetoxy-2,7-octadiene, mol	0.2	0.2	0.2
Additive			
Kind	Ti(OC ₄ H ₉) ₄	TiCl ₄	pheno-thiazine
mg	34	190	34
Reaction temp., °C	110	120	110
Reaction period, hr	1	1	1
*1 Conversion, %	84.7	42.3	66.5
*2 Selectivity, %	81.3	100	72.0
*3 n/iso ratio	1.48	1.56	1.79

Note: *1 Conversion of 1-acetoxy-2,7-octadiene.

*2 Selectivity of reaction products comprising normal type-compound and iso type-compound.

*3 Ratio of normal type-compound produced to iso type-compound produced.

Example 3

5 The same method as in Example 1 was followed for reacting 5.4 g (0.1 mol) butadiene with 16.8 g (0.1 mol) 1-acetoxy-2,7-octadiene, both being in solution in a variety of solvents, in the presence of 0.065 g (0.25 mmol) RhCl₃·3H₂O in solution in 0.46 g (10 mmol)

ethanol. The following Table 2 shows the reaction conditions and the results of the reactions. The respective amounts of the catalyst, 1,3-butadiene and 1-acetoxy-2,7-octadiene employed in run 1 were twice as much as those employed in the other runs 2 to 9.

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TABLE 2

Run	Solvent		Reaction temp., °C.	Reaction period, hr.
	Kind	g		
1	acetic acid	12	120	1.5
2	acetone	16.8	120	2
3	ditto	16.8	110	4
4	benzene	16.8	120	2
5	methylene dichloride	16.8	120	2
6	tetrahydrofuran	16.8	120	2
7	acetonitrile	16.8	120	2
8	dimethyl formamide	16.8	120	3
9	dimethyl acetoamide	16.8	120	3

TABLE 2 (Continued)

Run	Conversion, %	Selectivity, %	n/iso ratio
1	83.7	96.0	1.44
2	57.1	98.3	2.35
3	23.2	100	1.52
4	88.7	64.7	1.84
5	83.0	74.4	1.63
6	84.3	92.8	1.37
7	69.0	80.4	1.66
8	35.4	88.7	2.61
9	39.4	96.7	2.94

Example 4

The same method as in Example 1 was followed, employing ethanol as solvent and adding a variety of phosphorus compounds to

the reaction system. The reaction conditions and the results of reaction are listed in Table 3.

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TABLE 3

Run	1	2	3	4
1,3-butadiene, mol	0.1	0.1	0.1	0.2
1-acetoxy-2,7-octadiene, mol	0.1	0.1	0.1	0.2
Catalyst RhCl ₃ ·3H ₂ O, g	0.065	0.065	0.065	0.052
Phosphorus compound,		$\text{P}(\text{-O-} \text{C}_6\text{H}_4 \text{)}_3 \quad \text{P}(\text{C}_6\text{H}_5 \text{)}_3 \quad \text{P}(\text{C}_6\text{H}_5 \text{)}_3$		
Kind	P(n-C ₄ H ₉) ₃			
mmol	0.18	0.25	0.27	0.2
Solvent Ethanol, g	16.8	16.8	16.8	0.92
Reaction temp., °C	120	120	120	120
Reaction period, hr	8	6	3	6.5
Conversion, %	51.7	28.3	57.8	51.7
Selectivity, %	71.4	82.3	79.3	100
n/iso ratio	3.03	10.7	2.43	2.44

As shown in Table 3, the addition of phosphorus compounds to the reaction system resulted in increased n/iso ratios.

followed to effect the reaction, employing a variety of rhodium compounds other than $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ as catalyst. The reaction conditions and the results of reaction are shown in Table 4.

Example 5

5 The same method as in Example 1 was

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TABLE 4

Run	1	2	3
1,3-butadiene, mol	0.1	0.1	0.2
1-acetoxy-2,7-octadiene, mol	0.1	0.1	0.1
Catalyst			
Kind	RhBr_3	$\text{Rh}(\text{NO}_3)_3$	$[\text{Rh}(\text{OCOCH}_3)_2]_2$
mmol	0.25	0.5	0.2
Solvent			
Kind	ethanol	ditto	ditto
g	16.8	16.8	16.8
Reaction temp., °C	120	120	120
Reaction period, hr	6	3	3
Conversion, %	53.8	30.8	15
Selectivity, %	66.8	54.2	30

TABLE 4 (Continued)

Run	4	5	6
1,3-butadiene, mol	0.2	0.2	0.2
1-acetoxy-2,7-octadiene, mol	0.1	0.1	0.1
Catalyst			
Kind	$[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$	ditto	$\left[\text{Rh} \left(\text{Cyclo-octadiene} \right) \text{Cl} \right]_2$
mmol	0.025	0.025	0.05
Solvent			
Kind	acetic acid	trichloromethane	—
g	1.0	0.8	—
Reaction temp., °C.	120	120	120
Reaction period, hr	3	3	5
Conversion, %	10	8	5
Selectivity, %	ca. 100	ca. 100	ca. 100

Example 6

0.13 g (0.5 mmol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in solution in 0.92 g (20 mmol) ethanol were charged together with 16.8 g (0.1 mol) 1-acetoxy-2,7-octadiene into a 100 c.c. autoclave, 13.6 g (0.2 mol) isoprene were added thereto, and the mixture was reacted at 120°C for 3 hours, 30.2 g reaction liquor being obtained. The reaction liquor, after removal of unreacted isoprene by distillation, was composed of 8.2 g acetoxytridecatienes and 8.3 g 1-acetoxy-2,7-octadiene. Similarly to the acetoxydodecatiene produced in preceding Examples, the acetoxytridecatienes consisted of normal type-compounds and iso type-compounds in a 2.45 n/iso ratio.

Example 7

The same method as in Example 1 was followed for the reaction, substituting 1-methoxy-2,7-octadiene for 1-acetoxy-2,7-octadiene.

0.13 g (0.5 mmol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in solution in 0.92 g ethanol was charged together with

28.0 g (0.2 mol) 1-methoxy-2,7-octadiene into the 100 c.c. autoclave, about 11 g (0.2 mol) 1,3-butadiene were added thereto and the mixture was held at 120°C for reaction for 1.5 hours. Upon completion of the reaction, the autoclave was purged of unreacted 1,3-butadiene to give 36.2 g reaction liquor. The reaction liquor was distilled to recover 13.2 g unreacted 1-methoxy-2,7-octadiene, whilst obtaining 15.8 g of a fraction at a temperature of 55—64°C/0.012 mm Hg. Analyses by means of gas-chromatography and mass spectroscopy showed that the fraction was an isomeric mixture comprising 1-methoxy-2,6,10 - dodecatienes, 1 - methoxy - 2 - (2'-butenyl) - 3,7 - octadiene and 1 - methoxy - 2 - (2' - butenyl) - 2,7 - octadiene with a 1.5 n/iso ratio. Accordingly, it was calculated that the conversion of 1-methoxy-2,7-octadiene was 53%, and the selectivity of methoxy dodecatiene was 77% for the sum of normal type- and iso type-compounds.

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Example 8

The same method as in Example 7 was followed, substituting 1-phenoxy-2,7-octadiene for 1-methoxy-2,7-octadiene.

- 5 0.13 g $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in solution in 1.84 g ethanol and 20.2 g (0.1 mol) 1-phenoxy-2,7-octadiene were charged into the 100 c.c. autoclave, about 11 g 1,3-butadiene were added thereto, and the mixture was held at 120°C for reaction for 2.5 hours. Upon completion of the reaction, unreacted 1,3-butadiene was purged from the autoclave, leaving 30.2 g of reaction liquor. The reaction liquor was washed with water, dried with sodium sulphate, and subjected to active carbon treatment. The filtrate was distilled to recover 3.5 g unreacted 1-phenoxy-2,7-octadiene whilst 9.1 g of a fraction was obtained at 113—143°C/1.5 mm Hg. The fraction was analysed by the same means as in Example 7 and was found to be an isomer mixture consisting of 1-phenoxy-2,6,10-dodecatriene, 1-phenoxy-2-(2'-butenyl)-3,7-octadiene and 1-phenoxy-2-(2'-butenyl)-2,7-octadiene, having a 1.0 n/iso ratio. The conversion of 1-phenoxy-2,7-octadiene was 83%, and the selectivity for phenoxy dodecatrienes was 45%.

Example 9

- 30 The same method as in Example 7 was followed to effect the reaction, substituting 1-hydroxy-2,7-octadiene for 1-methoxy-2,7-octadiene.

- 35 0.065 g $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in solution in 0.46 g ethanol, 12.6 g benzene and 12.6 g (0.1 mol) 1-hydroxy-2,7-octadiene were charged into the 100 c.c. autoclave together, about 6 g (0.11 mol) 1,3-butadiene were added thereto, and the mixture was held at 120°C for reaction for 7 hours. Upon completion of the reaction, unreacted 1,3-butadiene was purged from the autoclave, and the reaction liquor was distilled

to recover 2.5 g unreacted 1-hydroxy-2,7-octadiene and to obtain 9.2 g of a fraction of a fractionation temperature 82—91°C/1 mm Hg. Analysis in the manner used in Example 7 showed that the fraction was a mixture consisting of 1-hydroxy-2,6,10-dodecatriene, 1-hydroxy-2-(2'-butenyl)-2,7-octadiene, and 1-hydroxy-2-(2'-butenyl)-3,7-octadiene having a 4.0 n/iso ratio. The conversion of 2,7-octadienyl-1-ol was 80%, and the selectivity for dodecatrienols was 64%.

Example 10

In this example 3-acetoxy-1,7-octadiene was employed in place of 1-acetoxy-2,7-octadiene for the reaction effected as in Example 1.

0.13 g $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in solution in 0.92 g ethanol and 33.6 g (0.2 mol) 3-acetoxy-1,7-octadiene were charged into the 100 c.c. autoclave, 10.8 g (0.2 mol) 1,3-butadiene were added, and the mixture was held at 110°C for reaction for 3 hours. Upon completion of the reaction, unreacted 1,3-butadiene was purged from the autoclave, leaving 43.7 g reaction liquor. The liquor was distilled to recover 19.6 g unreacted 3-acetoxy-1,7-octadiene and to obtain 11.6 g of a fraction at a fractionation temperature 67—79°C/0.005 mm Hg. Analyses by means of gas-chromatography and mass spectrum indicated that the fraction was acetoxy-dodecatriene. The distillation residue was a mixture of polymer and tarry substances. The conversion of 3-acetoxy-1,7-octadiene was 41.8%, and the selectivity for acetoxy-dodecatriene 62.3%.

Example 11

The same method as in Example 10 was followed, employing a variety of solvents for the reaction. The reaction conditions and the results of the reaction are listed on the following Table 5.

TABLE 5

Run	1		2		3
1,3-butadiene, mol	0.2		0.2		0.2
3-acetoxy-1,7-octadiene, mol	0.1		0.1		0.1
RhCl ₃ ·3H ₂ O, mol	0.5		0.5		0.5
Solvent					
Kind	Ethanol	Benzene	Ethanol	Methylene dichloride	Acetone
g	0.92	16.8	0.92	16.8	16.8
Reaction temp., °C	110		110		120
Reaction period, hr	3		3		3
Conversion, %	46.8		41.5		32.0
Selectivity, %	59.3		42.2		80.8

Example 12

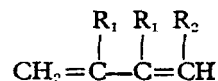
The same method as in Example 1 was followed, substituting 1,3,7-n-octatriene for 1,3-butadiene.

- 5 0.13 g (0.5 mmol) RhCl₃·3H₂O in solution in 0.92 g ethanol was charged along with 16.8 g (0.1 mol) 1-acetoxy-2,7-octadiene into the 100 c.c. autoclave, 10.8 g (0.1 mol) 1,3,7-n-octatriene were added thereto, and the mixture was held at a temperature of 105—115°C for reaction for 6 hours. The reaction liquor was distilled to recover 7.2 g unreacted 1-acetoxy-2,7-octadiene, 6.8 g of a fraction being also obtained at a fractionation temperature of 133—145°C/1 mm Hg. The fraction analysed by means of gas-chromatography and mass spectrum was found to be a mixture of isomers of acetoxy-hexadecatetraene.

the reaction liquor indicated the production of a C₁₆ tetraene containing an acetoxy group in about 6% yield.

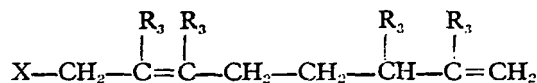
WHAT WE CLAIM IS:—

1. A method for the production of an alkapolypenyl group containing substance in which a molecule of a 1,3-conjugated diene is linked to an alkadienyl group containing compound and which substance has at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, which comprises reacting (i) a 1,3-conjugated diene represented by the formula

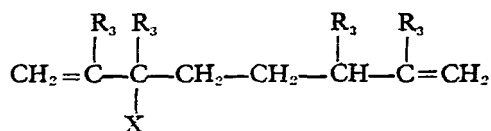


- 20 Example 13
The same method as in Example 12 was followed for the reaction, substituting 3-acetoxy-1,7-octadiene for 1-acetoxy-2,7-octadiene. The reaction was continued for 8
25 hours. A gas-chromatographic analysis of

in which the R₁'s may be the same or different and each denotes hydrogen or an alkyl group, and R₂ denotes hydrogen, an alkyl group or an alkenyl group, with (ii) an alkadienyl group containing compound which is a 1-substituted-2,7-alkadiene represented by the formula



or a 3-substituted-1,7-alkadiene represented by the formula



in which the R_3 's may differ from one another, each R_3 denoting hydrogen or an alkyl group, and X denotes a hydroxy group, an alkoxy group, an aryloxy group or an acyloxy group, the reaction being carried out in the presence of a rhodium compound as catalyst.

2. A method according to claim 1, in which the alkadienyl group containing compound is a 1-substituted-2,7-octadiene.

3. A method according to claim 1, in which the alkadienyl group containing compound is a 3-substituted-1,7-octadiene.

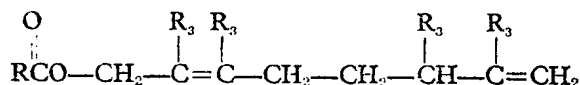
4. A method according to any one of

claims 1 to 3, in which the 1,3-conjugated diene is 1,3-butadiene.

5. A method according to any one of claims 1 to 3, in which the 1,3-conjugated diene is isoprene.

6. A method according to any one of claims 1 to 3, in which the 1,3-conjugated diene is 1,3,7-octatriene.

7. A method for the production of an alkapolienyl group containing ester having at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, which comprises reacting an alkadienyl ester represented by the formula



in which R denotes an alkali group or an aryl group and each R_3 denotes hydrogen or an alkyl group, the R_3 's being the same or different, with 1,3-butadiene, isoprene or a straight-chain dimer of 1,3-butadiene or isoprene, the reaction being carried out in the presence of a rhodium compound as catalyst.

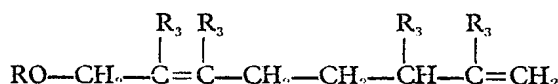
8. A method according to claim 7, in which a 1-acyloxy-2,7-octadiene, is reacted with 1,3-butadiene.

9. A method according to claim 7, in which a 1-aryloxy-2,7-octadiene is reacted with isoprene.

10. A method according to claim 7, in which a 1-acyloxy-2,7-octadiene is reacted with 1,3,7-octatriene.

11. A method according to any one of claims 7 to 10, in which the alkadienyl ester is 1-acetoxy-2,7-octadiene.

12. A method for the production of an alkapolienyl group containing ether having at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, which comprises reacting an alkadienyl ether represented by the formula



in which R denotes an alkyl group or an aryl group, and each R_3 denotes hydrogen or an alkyl group, the R_3 's being the same or otherwise, with 1,3-butadiene, isoprene or a straight-chain dimer of 1,3-butadiene or isoprene, the reaction being carried out in the presence of a rhodium compound as catalyst.

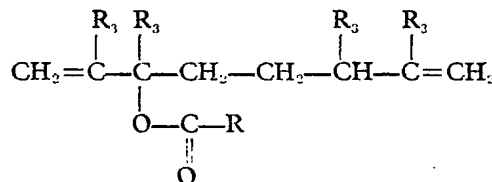
13. A method according to claim 12, in which a 1-alkoxy-2,7-octadiene is reacted with 1,3-butadiene.

14. A method according to claim 12, in which a 1-aryloxy-2,7-octadiene is reacted with 1,3-butadiene.

15. A method according to claim 12 or claim 13, in which the alkadienyl ether is 1-methoxy-2,7-octadiene.

16. A method according to claim 12 or claim 14, in which the alkadienyl ether is 1-phenoxy-2,7-octadiene.

17. A method for the production of an alkapolienyl group containing ester having at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, which comprises reacting an alkadienyl ester represented by the formula

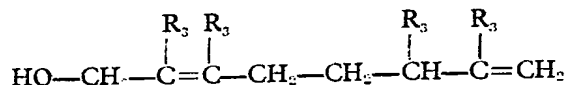


in which R denotes an alkyl group or an aryl group, and each R_3 denotes hydrogen or an alkyl group, the R_3 's being the same or otherwise, with 1,3-butadiene, isoprene or a straight-chain dimer of 1,3-butadiene or isoprene, the reaction being carried out in the presence of a rhodium compound as catalyst.

18. A method according to claim 17, in which a 3-acyloxy-1,7-octadiene is reacted with 1,3-butadiene.

19. A method according to claim 17, in which a 3-acyloxy-1,7-octadiene is reacted with 1,3,7-octatriene.

- 5 20. A method according to any one of claims 17 to 19, in which the alkadienyl ester is 3-acetoxy-1,7-octadiene.



- 15 in which each R_3 is hydrogen or an alkyl group, the R_3 's being the same or otherwise, with 1,3-butadiene, isoprene or a straight chain dimer of isoprene or 1,3-butadiene, the reaction being carried out in the presence of a rhodium compound as catalyst.

- 20 22. A method according to any one of the preceding claims, in which the rhodium compound is an inorganic salt.

23. A method according to claim 22, in which the rhodium compound is rhodium chloride.

- 25 24. A method according to claim 22, in which the rhodium compound is rhodium bromide.

- 30 25. A method according to any one of claims 1 to 21, in which the rhodium compound is an organic salt of rhodium.

26. A method according to any one of claims 1 to 21, in which the rhodium compound is a rhodium complex.

- 35 27. A method for the production of acetoxydodecatriene, which comprises reacting 1,3-butadiene with 1-acetoxy-2,7-octadiene in the presence of rhodium chloride as catalyst.

- 40 28. A method for the production of methoxydodecatriene, which comprises reacting 1,3-butadiene with 1-methoxy-2,7-octadiene in the presence of rhodium chloride as catalyst.

- 45 29. A method for the production of phenoxydodecatriene, which comprises reacting 1,3-butadiene with 1-phenoxy-2,7-octadiene in the presence of rhodium chloride as catalyst.

- 50 30. A method for the production of dodecatrienol, which comprises in reacting 1,3-butadiene with 1-hydroxy-2,7-octadiene in the presence of rhodium chloride catalyst.

- 55 31. A method according to any one of the preceding claims, in which the reaction is carried out at a temperature of from 50° to 250°C.

- 60 32. A method according to any one of the preceding claims, in which the reaction is effected at a temperature in the range 70—200°C.

33. A method according to any one of the preceding claims, in which the reaction is effected at a temperature in the range 100—130°C.

- 65 34. A method according to any one of the preceding claims, in which the reaction is effected under autogenous pressure.

21. A method for the production of an alkapolienyl group containing alcohol having at least 12 carbon atoms and at least 3 carbon-carbon double bonds in the molecule, which comprises reacting an alkadienyl alcohol having the formula

35. A method according to claim 7, substantially as hereinbefore described with reference to any one of Examples 1 to 6 and 12.

36. A method according to claim 17, substantially as hereinbefore described with reference to Example 10 or Example 11.

37. A method according to claim 12, substantially as hereinbefore described with reference to Example 7 or Example 8.

38. A method according to claim 21, substantially as hereinbefore described with reference to Example 9.

39. A polyene whenever obtained by the method claimed in any one of the preceding claims.

40. 1 - Acyloxy - 2,6,10 - dodecatrienes.

41. 1 - Acetoxy - 2,6,10 - dodecatriene.

42. 1 - Acyloxy - 2 - alkenyl - 3,7 - octadienes.

43. 1 - Acyloxy - 2 - (2' - butenyl) - 3,7-octadienes.

44. 1 - Acetoxy - 2 - (2' - butenyl) - 3,7 - octadiene.

45. 1 - Acyloxy - 2 - alkenyl - 2, 7- octadienes.

46. 1 - Acyloxy - 2 - (2' - butenyl) - 2,7 - octadienes.

47. 1 - Acetoxy - 2 - (2' - butenyl) - 2,7 - octadiene.

48. 1 - Alkoxy - 2,6,10 - dodecatrienes.

49. 1 - Methoxy - 2,6,10 - dodecatriene.

50. 1 - Alkoxy - 2 - alkenyl - 3,7 - octadienes.

51. 1 - Methoxy - 2 - (2' - butenyl) - 3,7 - octadiene.

52. 1 - Alkoxy - 2 - alkenyl - 2,7 - octadienes.

53. 1 - Methoxy - 2 - (2' - butenyl) - 2,7 - octadiene.

54. 1 - Aryloxy - 2,6,10 - dodecatriene.

55. 1 - Phenoxy - 2,6,10 - dodecatriene.

56. 1 - Aryloxy - 2 - alkenyl - 3,7 - octadienes.

57. 1 - Phenoxy - 2 - (2' - butenyl) - 3,7 - octadiene.

58. 1 - Aryloxy - 2 - alkenyl - 2,7 - octadienes.

59. 1 - Phenoxy - 2 - (2' - butenyl) - 2,7 - octadiene.

60. 1 - Hydroxy - 2,6,10 - dodecatriene.

61. 1 - Hydroxy - 2 - alkenyl - 3,7 - octadienes.

62. 1 - Hydroxy - 2 - (2' - butenyl) -
3,7 - octadiene.
63. 1 - Hydroxy - 2 - alkenyl - 2,7 - 53—64 Chancery Lane, London, WC2A 1SD.
octadienes. Agents for the Applicants.
- 5 64. 1 - Hydroxy - 2 - (2' - butenyl) - 2,7 -
octadiene.

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